METC/CR-79/5
Distribution Category UC-90a

USE OF WEIGHTED X-RAY DIFFRACTION DATA FOR SEMI-QUANTITATIVE ESTIMATION OF MINERALS IN LOW-TEMPERATURE ASHES OF BITUMINOUS COAL AND IN SHALE

February 1979

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Prepared for

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, WV

By

West Virginia University
and
West Virginia Geological and Economic Survey
Morgantown, WV

Under

Contract No. EY-76-C-05-5199

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ABSTRACT

The intensity of x-rays diffracted from a component of a mixture is proportional to the concentration of that component in the mixture. The proportionality constant is however affected by various parameters including sample preparation and mounting, equipment operation, the composition and crystallinity of the component and the overall composition of the mixture to name just a few. Assuming critical control of sample preparation, mounting and equipment operation, for a specific sample type, weighting factors were determined which when applied to the observed x-ray intensities of the individual minerals allowed a reasonably accurate semiquantitative estimation of the mineral abundances to be calculated. The effectiveness of the weighting factors was evaluated using both parametric and non-parametric statistical comparisons with other conventional analytical procedures. Because the sample preparation and mounting procedures are critical for the success of this or any other analytical technique, the procedures used are detailed.

ACKNOWLEDGEMENTS

The author would like to express his appreciation to other members of the staff of the West Virginia Geological Survey who contributed to this paper including Robert Romanosky and Edward Nuhfer who provided elemental analysis and to Michael Hohn and Hobart King who directed the statistical evaluation of the data.

INTRODUCTION

Semi-quantitative mineralogical analysis by x-ray diffraction is based upon the relationship that the integrated intensity of an individual Bragg reflection from a mineral is proportional to the concentration (weight or volume percent) of that mineral in a mixture. The difficulty in applying this relationship in practice is the evaluation of the proportionality constant relating integrated intensity and concentration.

The magnitude of the proportionality constant is affected by what appears to be an endless list of factors. For the purpose of this discussion, these factors can be categorized into two basic groups. The first group would include all factors which arise from sample preparation, sample mounting technique and the particular geometry and operation of the equipment used. The second group would include those factors determined by the sample itself; namely the composition, crystal structure and crystallinity of the individual minerals and the overall elemental composition of the sample. The contributions of group one factors to the intensity of diffraction can be maintained reasonably constant by critical control of sample preparation and mounting and by the use of well maintained, stable equipment. The contribution of greatest concern, therefore, are those from group two; the sample itself. The success of a quantitative XRD technique will be determined in large part by how well sample based factors affecting diffraction intensity can be monitored and evaluated.

The total intensity of diffraction from a mineral is a function of the composition, crystal structure and degree of internal ordering (crystallinity) of the mineral. Because by definition no two minerals can have the same composition and crystal structure, the total intensity of diffraction from individual minerals in a mixture will not necessarily be proportional to the relative concentration of the minerals in the mixture. Furthermore, in quantitative XRD procedures, the concentration of a mineral is not evaluated based upon the total integrated intensity of diffraction but rather on the integrated intensity of a selected Bragg reflection. As a result, the proportionality constants relating integrated intensity and concentration for individual minerals in a mixture will not be the same although under certain conditions, because of the specific choice of Bragg reflection and the particular combination of composition, crystal structure and crystallinity, the proportionality constants for certain minerals may be quite similar.

In addition, the intensity of diffraction of all the minerals in a mixture will be affected by the overall elemental composition of the mixture depending upon the degree to which the mixture absorbs the incident and diffracted x-ray beams. In other words, it will depend upon the "mass absorption coefficient" of the mixture for the wave length of the radiation used. Because the overall composition will vary from sample to sample thereby affecting the intensity of the individual Bragg reflections, the absorption effect must be taken into account.

It is not the purpose of this paper to present a comprehensive review of quantitative x-ray diffraction techniques. However, a general reference to quantitative x-ray diffractometry can be found in Klug and Alexander (1954). Basic approaches to mineral quantification in various kinds of rock samples can be found in works such as those of Johns et al (1954), Schultz (1960), Schultz (1962), Diebold et al (1963), Cubitt (1975), and Renton (1977).

ANALYTICAL PROCEDURE

The basic procedure discussed in this paper employs weighting factors which serve to take into account the differences in the intensity of diffraction of individual minerals. The purpose of the weighting factors is to modify the intensity values of the selected Bragg reflections of minerals in a sample such that the proportionality constants between the intensities and the concentrations of all the minerals in the sample are of the same magnitude. If the data are then normalized by summing the individual weighted intensities and dividing the individual intensities by the intensity sum, a value is obtained, the percent total intensity (%T.I.), which is numerically equivalent to the concentration of the mineral in the sample. This normalization procedure also serves to monitor overall changes in the composition of the sample.

It is important at this time to point out that the magnitude of the individual weighting factors are critically dependent upon certain criteria:

(a) They are dependent upon the lithology of sample to be analyzed. A weighting factor applied to the intensity of the 3.34 Å line of quartz in a shale will not be the same as the weighting factor applied to the same line of quartz in a low temperature ash of coal or in a limestone. In fact, the weighting factors determined for a particular shale formation may not apply to another shale formation.

(b) The weighting factors will be dependent upon the type of sample mounting procedure. Weighting factors determined for samples prepared as pressed pellets may not be the same as samples prepared as slurry mounts on glass slides.

(c) The dependence upon the particular Bragg reflection selected is obvious. The weighting factor for the 3.34 Å line quartz would not be the same as that for the 4.27 Å line.

(d) The specific geometry of the diffractometer used for analysis will influence the weighting factors largely dependent upon whether or not the goniometer employs fixed or automatic adjusting divergence slits.

EVALUATION OF WEIGHTING FACTORS

The evaluation of weighting factors requires a series of samples for which both XRD data and elemental analyses are available. The x-ray data for each sample include the intensities of the specific Bragg reflections chosen as the analytical line for each mineral. The Bragg reflections chosen in this study are summarized in Table 1. The XRD data for each sample are first used to provide a list of minerals present in the sample. Using elemental concentrations calculated from standard formula of the individual minerals (see Table 2), and the analytical elemental data, a normative type analysis is performed for each sample whereby the concentration of each mineral in that sample is calculated based upon the available elemental concentrations. An elemental "analysis" is then calculated for each sample from these calculated mineral concentration data and compared to the analytical elemental data. The procedure

Table 1. Selected Analytical Bragg Reflections

Mineral	"d"	(hkl)	$^{0}2\theta$,CuK$_{\alpha}$
Chlorite *	14Å	001	6.2^{0}
Chlorite **	7Å	002	12.30^{0}
Illite	10Å	001	8.85^{0}
Coquimbite	8.26Å	101	10.71^{0}
Kaolinite	7.1Å	001	12.30^{0}
Gypsum	7.56Å	020	11.70^{0}
Anhydrite	3.49Å	002,020	25.50^{0}
Szmolnokite	3.44Å	111,200	25.90^{0}
Quartz	3.34Å	101	26.66^{0}
Orthoclase	3.24Å	040,002	27.50
Plagioclase	3.20Å	204	27.85^{0}
Calcite	3.04Å	104	29.35^{0}
Bassanite	3.00Å	200	29.75^{0}
Dolomite	2.90Å	104	30.85^{0}
Siderite	2.80Å	104	32.00^{0}
Pyrite/Marcasite	2.71Å	200	33.05^{0}

* Used with Siemens & Philips DMS 41 units
** Used with Philips APD 3500 unit

Table 2. Mineral Elemental Concentrations in Weight Percent

Mineral	Si	Al	Fe	Mg	Ca	K
Quartz	46.74					
Kaolinite	21.76	20.9				
Illite	23.8	13.5	3.1	1.8	0.28	5.4
Coquimbite			19.88			
Szmolnokite			32.87			
Gypsum					23.3	
Bassanite					27.6	
Anhydrite					29.4	
Calcite					40.0	
Dolomite				13.0		
Siderite			48.20			
Pyrite			46.55			
Chlorite	10.06	6.64	33.45	14.56		
Plagioclase	20.1	19.4			7.2	
Orthoclase	30.3	9.7				14.0

continues by adjusting the mineral concentrations until the calculated elemental analysis is the same as the analytical elemental analysis. The elements considered in this study were Si, Al, Fe, Mg, Ca and K. Rarely is a perfect match achieved for all the elements; Mg and Ca being in this study the most difficult elements to balance. However, when reasonably good matches were achieved for Si, Al, Fe and K, the calculated mineral concentrations were considered good estimates of the true mineral concentrations for that sample.

Having calculated the mineral concentrations based upon the available elemental concentrations, the weighting factors were then determined by dividing the x-ray intensity values into the respective calculated mineral concentration. Because the weighting factors are relative numbers, the largest weighting factor (in this case, the weighting factor for illite) for each sample is made to equal 10 (or 100) and all the other weighting factors are changed proportionally.

This process is repeated for each sample after which the weighting factors calculated for each mineral in each sample are summed and averaged. The average weighting factors then become instrumental "constants" and are used to calculate the mineral concentrations in all subsequent samples by multiplying the mineral Bragg intensities by the corresponding weighting factor; summing the weighted Bragg intensities and calculating the percent of total intensity represented by each individual mineral's Bragg intensity. The average weighting factors used in this study are summarized in Table 3.

The author would emphasize once again that weighting factors are calculated for a specific sample Lithology, a specific mounting procedure, for the specific Bragg reflections chosen for analysis and for a particular piece of equipment. Factors such as those listed in Table 3 should not be accepted by the reader as useable in his/her laboratory even for the same types of samples, mounts, Bragg reflections and equipment until their validity is verified. In addition, weighting factors, once determined, should not be considered fixed but rather should be continuously updated as additional samples with elemental analyses become available. The statistical reliability of the weighting factors increases as the number of samples from which the factors are calculated increases.

Table 3. Weighting Factors Used In This Study

MINERAL	SHALES		COAL LTA
	Siemens-Philips DMS 41	Philips APD 3500	Siemens-Philips DMS 41
Chlorite	0.81	2.20	
Illite	10.00	100.00	10.00
Kaolinite			3.45
Coquimbite			3.88
Szmolnokite	3.70	7.19	3.88
Pyrite	5.70	6.95	6.67
Gypsum	3.70	7.67	3.22
Bassanite	0.92	7.52	1.24
Anhydrite			3.06
Calcite	4.85	4.55	
Dolomite	4.85	3.59	
Siderite	5.41	6.92	
Plagioclase	3.70	2.40	3.88
Orthoclase	3.70	2.40	3.88
Quartz	3.22	2.78	1.94

SAMPLE PREPARATION & MOUNTING TECHNIQUES

Because sample preparation and mounting are critical to the success of this technique, the procedures for preparation and mounting used in this study are detailed in Appendix I.

EQUIPMENT USED

Three different XRD units were used in this study. Two of the instruments were a Siemens Krystalloflex IV unit equipped with a horizontal diffractometer and a Philips DMS 41 unit equipped with a vertical diffractometer. Both diffractometers were equipped with fixed 1° divergence slits and graphite monochromators. The Siemens unit employed CuK_{α} radiation while the Philips unit used CoK_{α}. Numerous samples run on both units showed that there was no statistical difference in the relative intensity data provided by the two units.

The third XRD unit was a Philips APD 3500 automatic x-ray diffraction unit. The diffractometer was equipped with a 34 position automatic sample changer and an automatic adjusting divergence slit. Graphite monochromated CuK_{α} radiation was used. All analyses were conducted using the Peak Search Mode of operation.

X-RAY ANALYSIS

<u>COAL LTA'S:</u> Coal LTA's were analyzed using the Siemens Krystalloflex IV and Philips DMS 41 units interchangeably. All scans were made at 1° 2θ per minute and chart presentations were 1° 2θ per centimeter for the Siemens unit and 2° 2θ per inch for the Philips unit. All intensity measurements were integrated intensity. Scans in both units were from approximately the 20 Å position up to and including the 2.71 Å pyrite-marcasite line. When a pyrite-marcasite differentiation was required, the scans were extended to include the 1.63 Å line of pyrite. Petrographic analysis of the coals used in this study showed that the only iron disulphide present was pyrite. A characteristic of most pyrite found in coal is that the 2.71 Å line is usually more intense than the 1.63 Å line. (Work being presently conducted indicates that this is not the result of preferred orientation.) For that reason, the 2.71 Å line was chosen

as the analytical line for pyrite.

In the coal LTA's analyzed, the major clay minerals were illite and kaolinite; no 14 Å clays were observed. When present, the 14 Å clay in bituminous coals has always been iron rich chlorite as identified by the strong (004) reflection and subsequent heat treatment. In such cases, the intensity contribution of the (002) chlorite reflection to the 7 Å position is calculated as twice the measured 14 Å (001) chlorite peak intensity. This value is subtracted from the intensity of the 7 Å position to provide the analytical kaolinite intensity.

SHALES: All samples were scanned from approximately 20 Å to approximately 1.5 Å (60° 2θ with CuK_α and 70° 2θ with CoK_α). With the Siemens Krystalloflex II and Philips DMS 41 units, all scans were made at 1° 2θ per minute with chart presentations of 1° 2θ per centimeter and 2° 2θ per inch respectively. With the Philips APD 3500 unit, Peak Search Mode of operation was used, with a minimum peak/background ratio of 1.25, a count mode fixed time of 0.5 seconds, and a full scale chart presentation of 1000 counts. Each series of samples was calibrated on the quartz strong line at 26.66° 2θ. Integrated intensity measurements were made on the diffractograms from the Siemens and Philips DMS 41 units using the product of the peak height times the width of the peak at one-half the height. The Peak Search Mode of operation of the APD 3500 provides absolute intensity measurements.

The samples analyzed in this study were part of the D.O.E. Eastern Devonian Gas Shales Project. The major clay minerals were illite and iron rich chlorite. Kaolinite has been identified in a few of the shale samples from the project in minor concentrations but was not present in any of the samples described here. In samples which do contain kaolinite, the proportions of the intensity of the 7 Å position attributed to the (002) reflection of chlorite and the (001) reflection of kaolinite were calculated proportional to the intensities of their 3.54 Å and 3.58 Å lines respectively.

EXPERIMENTAL DATA

The samples used in this study to test the calculated weighting factors include seven samples of Waynesburg coal representing a channel sampling of the entire seam at a local surface mine and eleven samples of shale taken from a core of the Devonian "Black Shale" as part of the D.O.E.

sponsored Eastern Devonian Gas Shales Project.

The suite of shale samples were specifically chosen, based upon available petrographic and elemental analyses, to represent as complete a range of shale compositional variability as was encountered in the D.O.E. study, i.e. any other sample or samples chosen would fall within the range of compositions represented by this suite. All samples were prepared, mounted and analyzed as previously outlined. The weighting factors listed in Table 3 were applied and %T.I. data were calculated. Using the %T.I. values as mineral concentrations and the elemental data summarized in Table 1, a set of calculated elemental analysis were generated and compared against analytical elemental data for the coal ashes. The data sets for coal are listed in Table 4 while the comparable shale are summarized in Table 5.

A visual comparison of the data shows for almost every element a close agreement between calculated and analytical values. The consistently high calculated Mg values in the case of the shales is probably because the Mg content of the "standard" chlorite (14.56%) was higher than that of the chlorite found in these samples. No explanation can be given for the poor comparison of the Ca data for the shales except that the calcium bearing minerals were all of low abundance and subsequently their x-ray intensity measurements would reflect the higher error involved in measuring low intensity peaks. In addition, the plagioclase feldspar in the shales was represented by 50:50 Ca:Na ratio in lieu of specific knowledge of its actual composition.

STATISTICAL TESTS TO EVALUATE ANALYTICAL ACCURACY

It is difficult and perhaps impossible to make a statistically sound evaluation of the analytical accuracy with which this technique estimates true mineral concentrations. The mineral concentration data (%T.I.) cannot be compared directly to a mineralogical analysis generated by another method because another method does not exist. The samples are too fine grained for accurate optical microscopic analysis and other instrumental techniques such as infrared spectroscopy are not sufficient quantitative for some of the major minerals, especially illite.

Three methods used were to evaluate the effectiveness of the proposed technique to quantitatively estimate mineral concentrations: (a) A comparison of calculated and analytical

Table 4. Calculated (C) and Analytical (A) Elemental Data for Coals

Si		Al		Fe		Mg		Ca		K	
C	A	C	A	C	A	C	A	C	A	C	A
22.76	25	13.68	14	3.85	3.7	0.77	0.64	0.44	0.73	2.38	1.9
21.87	23	14.36	12	4.03	3.1	0.44	0.61	0.33	0.73	1.41	2.6
24.04	21	11.85	12	3.95	8.5	0.54	0.62	0.88	0.35	1.77	1.9
23.05	23	10.87	10	6.34	5.7	0.59	0.50	1.13	1.00	1.93	1.9
24.24	23	11.58	10	5.43	5.7	0.47	0.50	0.67	1.00	1.58	1.9
23.68	22	12.51	13	4.78	4.3	0.72	0.57	0.55	0.65	2.16	2.2
20.26	21	9.71	11	12.22	15.0	0.49	0.50	0.85	0.57	1.69	1.6

Table 5. Calculated (C) and Analytical (A) Elemental Data for Shales

Si		Al		Fe		Mg		Ca		K	
C	A	C	A	C	A	C	A	C	A	C	A
27.10	27.0	9.44	8.34	4.81	4.73	1.44	1.10	0.93	0.90	3.70	3.03
28.63	25.8	7.42	8.49	6.35	5.70	1.12	1.00	0.99	0.37	2.85	3.05
28.29	27.4	7.75	8.09	4.08	3.86	1.42	1.36	2.54	2.87	3.00	3.16
26.21	26.0	9.55	9.40	3.63	4.53	1.43	1.17	0.75	0.93	3.59	3.65
21.37	20.9	6.61	6.56	1.81	3.52	1.27	1.04	12.94	13.09	2.47	2.72
26.88	24.5	7.06	8.83	8.89	7.59	0.95	0.96	0.98	0.17	2.59	2.70
26.12	27.4	9.41	9.14	3.81	3.85	1.48	1.21	0.68	0.51	3.44	3.22
27.53	27.2	8.67	7.94	5.19	5.15	1.18	1.02	1.42	0.16	3.23	2.83
25.30	26.9	7.20	7.64	7.14	4.47	1.01	1.04	0.89	1.17	2.58	2.71
27.35	25.3	9.12	8.97	2.77	6.68	1.24	1.03	0.80	0.51	3.20	3.14
25.27	26.6	9.79	9.59	5.16	4.40	1.33	1.16	1.06	0.20	3.55	3.59

elemental analyses, (b) A comparison of calculated and determined mineral concentrations, and (c) A comparison of calculated and measured matrix density.

COMPARISON OF CALCULATED AND ANALYTICAL ELEMENTAL ANALYSES

The first method statistically compared the mean values of the calculated and analytical elemental concentrations for both coal and shale samples. The fact that "standard" mineral formula were used to calculate the elemental data introduces a degree of uncertainty that is impossible to evaluate. The analytical elemental data themselves suffer from a certain degree of experimental error, while in addition, the original x-ray intensity data can only br reproduced to within 3 or 4 percent of a mean value. For all those reasons, the author will not attempt to transpose the statistical comparison of elemental means to any estimate of accuracy of the mineralogical determinations but rather will present the data and its statistical treatment and allow the reader to judge the effectiveness of the procedure to estimate the true mineral concentrations.

The calculated and analytical elemental data were compared by both parametric and non-parametric techniques. Plots of the data showed that with the exception of the Ca and Fe values of the shale data, all the elements showed mound-shaped probability distributions thereby justifying the use of the parametric Student's Test. However, because the number of samples involved were few and there exists therefore a justifiable question as to the normalcy of the data, non-parametric tests were included. The specific non-parametric tests used were the Wilcoxon Matched-Pairs-Signed-Ranks Test and the Mann-Whitney Test.

The Null hypothesis made in each case was that no difference existed between the calculated and analytical elemental analyses. The basis for the argument presented here is that if the null hypothesis cannot be rejected then it must be concluded that the calculated mineral concentrations are reasonably accurate estimates of the true mineral abundances. On the other hand, if the null hypothesis is rejected, the calculated concentrations cannot be good estimates of true mineral concentrations. A summary of the results of the tests for the coal data is given in Table 6.

Table 6. Summary of Statistical Data for Coal

	Statistical Test		
Element	Student's t	Wilcoxon	Mann-Whitney
Si	0.48	11	16
Al	0.83	11	22
Fe	-0.29	14	23
Mg	0.30	13	21
Ca	0.37	13	22
K	-0.67	10	18

The conditions for rejection of the H_o and the corresponding confidence levels are summarized below:

Test	Confidence Level	Cond. for Rejection of H_o
Student's t	90% C.L.	t = 1.943
Wilcoxon	95% C.L.	Critical Value = 2
Mann-Whitney	90% C.L.	$U \leq 14$

At the confidence levels indicated, the H_o could not be rejected. Furthermore, it might be pointed out that in the case of the Student's t Test, the H_o could not be rejected for any element at the 80% confidence level (t = 1.440). It is therefore concluded that the procedure provides reasonably accurate estimations of the true mineral abundances in the low temperature ash of bituminous coal.

Table 7. Summary of Statistical Data for Shales

	Statistical Test		
Element	Student's t	Wilcoxon	Mann-Whitney
Si	1.09	21	49.5
Al	-0.36	33	60
Fe	-0.13	29	58
Mg	4.55	3	29
Ca	2.09	20	37.5
K	0.39	29	56.5

The conditions for rejection of the H_o and the corresponding confidence levels are summarized below:

Test	Confidence Level	Cond. for Rejection of H_o
Student's t	90% C.L.	t = 1.812
Wilcoxon	95% C.L.	Critical Value = 11
Mann-Whitney	90% C.L.	$U \leq 34$

The H_o was rejected by the Student's Test for Mg and Ca for the reasons previously discussed. However, it is important to note that the elemental means of Si, Al, Fe and K were not rejected at the indicated confidence levels. The means of Si, Al, Fe and K were, in fact, indicated to be statistically the same at the 80 percent confidence level (t = 1.372).

The Mg data were also shown to be statistically different by the non-parametric tests, but the Ca data were not. Based upon the statistical similarity of the calculated and analytical values for Si, Al, Fe and K (and Ca according to the non-parametric tests), it is concluded that the procedure provides reasonably accurate estimates of the true mineral abundances in the shale samples.

Using the weighting factors listed, the average sum of the calculated mineral concentrations was 98% for the shales and 96% for the coals.

COMPARISON OF CALCULATED AND DETERMINED MINERAL ABUNDANCE

A second method used to evaluate the effectiveness of the weighted intensity procedure in the quantification of minerals in a shale sample was to compare the concentration of quartz determined using the weighted x-ray intensities and the quartz concentration determined by the method of additions (M.O.D.).

It must be pointed out however, that the use of the M.O.D. procedure for quantification of any mineral species makes certain assumptions that more than likely will not be met. It assumes, for example, that the composition and degree of crystallinity of the added "standard" mineral is the same as that of the mineral to be quantified in the samples; it is highly unlikely that this is the case. "Standard" minerals are usually selected museum grade specimens whose purity of composition and high degree of crystallinity are rarely duplicated in natural samples. This, of course, is the shortcoming of all techniques using "standard" minerals. In addition, the method of additions cannot take into account that there will be variations in composition and degree of crystallinity in both the "standard" mineral as well as the mineral as it occurs in the samples. Quartz was chosen to be quantified because in the opinion of the author, it would be the one mineral in the samples which would show the least deviation from the ideal composition and the least variability in degree of crystallinity and as such would be the most likely mineral phase to be duplicated by the composition and degree of crystallinity of a "standard" mineral sample.

The "standard" quartz chosen was Brazilian quartz ground, prepared and mounted by the exact same procedure outlined for the samples (see Appendix I). To test the variability in the x-ray diffraction data for the "standard" quartz, seven separate samplings of the Brazilian quartz, all identically prepared, were scanned for the 3.34 Å strong line on the Philips APD 3500. The intensities of the 3.34 Å line for the seven samples ranged from 59K counts full scale to 76K counts full scale with the individual intensities being 59K, 62K, 75K, 75K, 75K, 75K, and 76K counts full scale. A single sample mount replicated on the APD 3500 provided data which replicated within 3 or 4 percent of a mean value. These data point up the variability in the "standard" mineral data whether it be the result of variability within the material itself or uncontrollable variability within the preparation and mounting procedure.

Seven additional shale samples were chosen at random for the test. For each sample, seven separate mounts were prepared which included the sample itself, five mixtures of the sample containing 10%, 20%, 30%, 40% and 50% respectively of the "standard" quartz and a mount of the "standard" quartz itself (100% quartz). For each of the seven mounts of each sample, the intensities of the 4.27 Å and 3.34 Å lines of quartz, corrected for background, were determined. From these data, the concentration of quartz in each sample was determined by the method of additions. These concentration data were then compared to the quartz concentrations determined by the weighted intensities procedure. The comparison of data is illustrated in Figure 1. The MOD quartz concentration plotted in Figure 1 for each sample is the average of the concentrations determined by using both the 4.27 Å and the 3.34 Å Bragg reflections. The average difference between the two values determined by using the 4.27 Å and the 3.34 Å reflections was 4% with the concentration

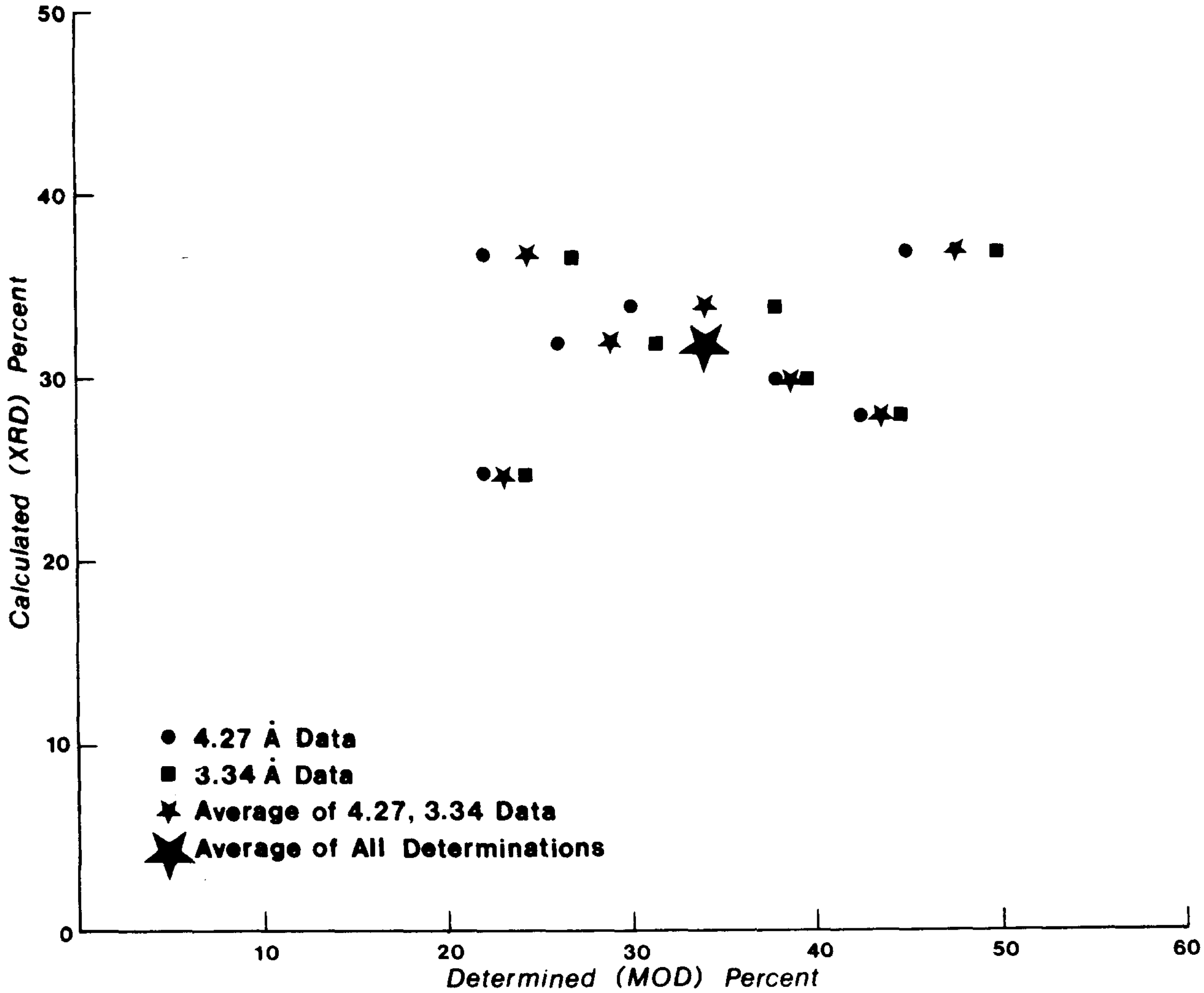

Figure 1. Comparison of Determined (MOD) and Calculated (XRD) Quartz Concentrations

determined using the 3.34 Å reflection intensities being consistently the higher of the two.

A statistical comparison of the two sets of data was made using the non-parametric Wilcoxon and Mann-Whitney Tests. The null hypothesis for both tests was that there was no difference between the two data sets. The null hypothesis could not be rejected using either test at the 95% confidence level. The conclusion is that the quantification of quartz in the samples using weighted intensities and by the method of additions procedure produce results which cannot be proven to be statistically different.

COMPARISON OF CALCULATED AND MEASURED MATRIX DENSITY

A third test involved a comparison of measured and calculated matrix densities (mineral plus organic matter) in 212 samples of shale. In this study all mineral concentrations were determined using the weighted x-ray intensity data except pyrite. Studies being conducted in this laboratory on pyrite occurrences in shale and coal indicate that signficant variations in x-ray diffraction intensities for pyrite result from apparent variations in pyrite stoichiometry, morphology and/or crystallinity. Because pyrite is a major contributor to the density of any sample, the potential error in density values based upon XRD data necessitated an alternative method of estimating the concentration of pyrite. The method used was to calculate the pyrite concentration from a pyritic sulfur analysis.

The measured and calculated matrix density values for the 212 samples were compared using the non-parametric Wilcoxon 2 Sample Test and the Student's Test. The null hypothesis for both tests was that no difference between the two sets of data. The null hypothesis of no difference between the two sets of data was rejected at the 95% confidence level. However, a comparison was made of the difference between the calculated and measured matrix densities with the difference calculated as a percentage of the measured matrix density value. The mean difference between the calculated and measured values was 2.55% with only 12 of the 212 samples showing a difference of 10% or more. The mean measured matrix density for the 212 samples was 2.72 while the mean calculated matrix density was 2.78. Although the data were not good enough to allow acceptance of the null hypothesis, when one considers all the potential errors involved in a calculated matrix density value, the original estimate of the mineral abundances could not have been far off in order to provide the observed close agreement.

One further point need be made concerning the statistical tests performed in this paper. All of the tests were such that the object was to accept the null hypothesis of no difference. To reject the null hypothesis would have required the conclusion that the estimated mineral abundances were not good estimates of the true mineral abundances. The acceptance of the null hypothesis of no difference is not equivalent to saying the data are the same. However, when one considers the inherent lack of accuracy of the x-ray diffraction technique itself and the basic assumptions made in all of the tests presented in this paper, the fact that the statistical comparison of calculated and measured analytical parameter could not be proven statistically different would strongly argue for the estimated mineral abundances from which the calculated data were termed as being reasonably good estimates of the true mineral abundances.

CONCLUSIONS

The use of properly determined weighting factors with x-ray diffraction data allows a reasonably accurate estimate to be made of the mineral abundances in the low temperature ashes of bituminous coal and siliceous shale. It is reasonable to assume that the procedure could be extended to include other sample types.

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APPENDIX I

I. LOW TEMPERATURE ASH OF COAL

(a) SAMPLE PREPARATION: The low temperature ashes were generated by ashing 1 gram of -60 mesh coal in a commercial low temperature asher. The ashing was accomplished using 15 watts of power per ashing chamber. At this power setting, the maximum sample temperature observed by means of a Barnes Infrascope was less than 150°C. The samples were removed from the asher two or three times during a working day, weighed and stirred; ashing was usually complete for bituminous coals in 72 hours. Upon completion of the ashing, the ashes were prepared for XRD.

(b) SAMPLE MOUNTING: The pressed pellet technique was used exclusively for all LTA's. A Spex-cap was filled with the -60 mesh coal from which the ash was derived and packed firmly with a broad blade spatula to a smooth surface. The LTA was then spread over the coal surface, care being taken not to disturb the packed surface of the coal. A square of Saranwrap was placed over the cap. The purpose of the Saranwrap is to prevent the ash from sticking to the die platen during pressing. The loaded cap with the Saranwrap was centered on the lower die platen, the body of the die is lowered over the cap and lower platen so as not to displace the Saranwrap. The upper platen is then lowered into the die followed by the ram. The pellet was pressed at 15 ton total load for 2 minutes. The pressure was released, the die was rotated 180° and repressed at 15 ton total load for an additional 2 minutes. Upon removal from the die, the Saranwrap was carefully pealed from the sample surface and the pellet stored in a vacuum desiccator until analyzed.

II. SHALE

(a) SAMPLE PREPARATION: Shale samples were crushed by hand to a fine powder using a steel mortar and pestle. The powders were then further reduced using a Spex Mixer-mill and the 30 ml tool steel grinding vial equipped with a cap compression closure. The vial was filled approximately 1/3 full with the pulverized sample; 300 stainless steel balls and 25 ml of methanol were added and the vial was sealed. The sample was ground for 15 minutes. After grinding, the resultant slurry was poured through a screen to retain the stainless steel balls into evaporating dishes. The samples were then allowed to air dry. When dry, the samples were repulverized by hand and stored in sealed vials.

(b) SAMPLE MOUNTING: Two mounting techniques were used depending upon the specific instrument used for analysis.

1. PRESSED PELLET: Pellets were prepared by filling a Spex cap and pressing at a total load of 15 tons for 2 minutes. The pressure was released, the die turned 180° and the pellet repressed at 15 ton total load for an additional 2 minutes. The samples were then either stored under vacuum or in sealed bags with desiccant until analyzed.

2. FILTER MOUNT: Filter mounts were prepared using a Millipore Sterifil filtration assembly utilizing 47 mm 0.45 micron filters. One hundred milligrams of sample were dispersed in 100 ml of pH 10 water and stirred with a magnetic stirrer for 2 minutes. The filter assembly was prepared and the filter thoroughly wetted with distilled water. The suspended sample was then poured all at once into the filter reservoir and filtration was conducted under vacuum. Several washings with distilled water were added; care being taken not to disturb the sample cake. The mounted filters were then removed and allowed to air dry between paper towels. When dry, the filters can be mounted for analysis by affixing them to glass plates with double-backed Scotch tape. In this study, the filter mounts were analyzed exclusively on a Philips APD 3500 equipped with an automatic sample changer in which case the filters were affixed to the plastic sample mount with double-backed Scotch tape. The excess filter was carefully trimmed off and the plastic mount was placed in the metal holder.